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Rheological properties of poly(vinyl alcohol) (PVA) derived composite membranes for fuel cells

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Abstract. Rheological properties of new anhydrous proton conducting membrane based on PVA, tetraethyl orthosilicate (TEOS), sulfosuccinic acid (SSA), titanium dioxide (TiO_2) was examined at various stoichiometric ratios. SSA was used as sulfonating agents to form a crosslinked structure and as proton source, whereas TEOS and TiO_2 were utilized to improve the thermal and mechanical properties of the membrane. In order to verify that all the substances were immobilized into the matrix, the membranes were analysed by means of FT-IR. The rheological, mechanical and thermal properties of the membranes were investigated using rheometer ARES G2 and thermogravimetric analyser (TGA). The analysis of mixed PVA solutions exhibited a unique behaviour of viscosity with increased crosslink density. The dynamic storage modulus G' of dried composite membranes shows better mechanical resistance and increased tolerance to pressure applied during membrane electrode assembly (MEA).

1. Introduction

Hydrophilic PVA membranes are used in many applications, but lately they have been widely utilized as polymer electrolyte membrane (PEM) for fuel cells. In order to design a good membrane many parameters are involved, such as the properties of casting solution, preparation conditions (temperature, relative humidity and time), reactants etc. The viscosity of the polymer solution plays a key role, which not only helps to fabricate membranes of specific thickness, but also prevents the formation of pinholes and membrane delamination. Therefore, the understanding of the rheological properties of casting solutions is important for preparing appropriate membranes for fuel cells. In this study we have prepared conducting membranes based on PVA, TEOS, SSA, TiO_2 at various stoichiometric ratios and investigated the rheological properties.

2. Experimental

2.1. Material

PVA (hydrolyzed 99+%, $M_w = 86000\text{--}98000$), SSA (70 % in water), Titanium(IV) butoxide (97%) and were obtained from Sigma-Aldrich (USA). TEOS and hydrochloric acid (HCl, 37 wt %) were purchased from Merck Chemicals (Germany). All the chemicals were of analytical grade and used as received. Deionized water was utilized for all the membrane preparation experiments.



2.2. Membrane preparation

Composite PVA membranes were prepared by the solution casting method. At first, a 5 wt% solution of PVA in water was prepared by continuous stirring at 90 °C until the complete dissolution was achieved. The PVA solution was mixed with SSA for 24 h at room temperature. Further, TEOS mixture was prepared by mixing H₂O, HCL and TEOS in the molar ratio of 4:0.1:1, which was stirred at room temperature for 2 h [1] and added to the PVA-SSA solution. Subsequently, TiO₂ mixture was added to the solution and the stirring was continued at room temperature for 2 h. TiO₂ solution mixtures were prepared by mixing H₂O, HCL and Titanium(IV) butoxide in the molar ratio of 10:4:1. The composition of each solution is specified in Table 1. The prepared solution was poured into the automatic film applicator (TQC, Germany) equipped with a plexiglass plate and was fabricated into membranes with uniform thickness and dried at 40 °C.

2.3. Characterization

Dynamic TGA was used to evaluate the relative thermal stability of modified PVA membranes. The TGA curves were obtained with a TGA Q500 thermogravimetric analyser (TA Instruments, USA). Samples of about 5 mg were heated at a rate of 10 °C/min in N₂ atmosphere. The weight of the samples was measured as a function of temperature.

The rheological studies of the PVA solutions were measured on a rheometer ARES G2 from TA Instruments. The polymer solutions were inserted between two parallel plate geometries (d = 25 mm). For each measurement, the shear rate from 0.1 to 100 s⁻¹, for a duration 30 s was carried out at room temperature. Membranes were cut (d = 25 mm) and inserted between two parallel plate geometries (d = 25 mm). For these measurement angular frequency from 1 to 100 rad·s⁻¹, strain 5%, was used.

FTIR reflectance spectroscopy studies were performed on the samples using NICOLET 380-FTIR spectrometer, in a spectral range of 400 – 4,000 cm⁻¹.

Table 1. - Composition of polymer solution

Sample	Solution mixture
M1	5% PVA
M2	5% PVA_0.5% SSA
M3	5% PVA_1% SSA
M4	5% PVA_2% SSA
M5	5% PVA_3% SSA
M6	5% PVA_0.5% SSA_2.5% TEOS
M7	5% PVA_0.5% SSA_2.5% TEOS_0.1% TiO ₂

3. Results and discussion

3.1. FT-IR

Figure 1 shows the FT-IR spectra of the M1 and M7 membranes. It was reported that the absorption band of ester (–COO–) appeared at 1730–1735 cm⁻¹. These results indicate the spectral changes are an evidence of a crosslinking by the esterification between –OH in PVA and –COOH in SSA. The absorption band at 2369 cm⁻¹ indicate the presence of sulfonic acid group, which is formed by the introduction of SSA [2]. The band at approximately 1040 cm⁻¹ is assigned to stretching vibrations of Si–O–Si. The absorption band, at 900 cm⁻¹ can be attributed to the stretching vibration of Si–OH or Si–O– groups. A broad absorption band, situated between 3,000 and 3,600 cm⁻¹, are assigned to O–H stretching and O–H bending vibrations, respectively [3]. For the spectrum of TiO₂, the peaks at 1471 and 1645 cm⁻¹ show stretching vibration of Ti–O and Ti–O–Ti, respectively [5].

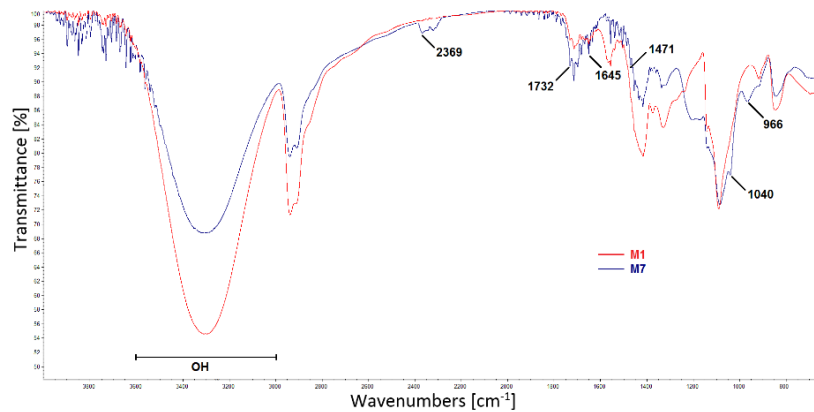


Figure 1. FT-IR spectra of composite PVA membranes

3.2. Rheology

The viscosity of the pure PVA solution changed after the incorporation of SSA (Figure 2). At low SSA content, the viscosity was initially increased due to the interaction between the acid groups of SSA and PVA. However, the viscosity was reduced slightly when the SSA loading percentage exceeded 0.5 wt%. The slight reduction in our observed viscosity can be explained by the limited dispersion behaviour of SSA in the PVA matrix. Agglomeration of particles resulted in the reduced surface area between the SSA and PVA, and caused the decrease in viscosity. The rheological properties of dried membranes were determined by means of shear experiments. Figure 3 shows the storage (G') modulus versus frequency curves of composite PVA membranes. The storage modules are in order as expected since each additional added component means higher crosslinking extents and better mechanical properties.

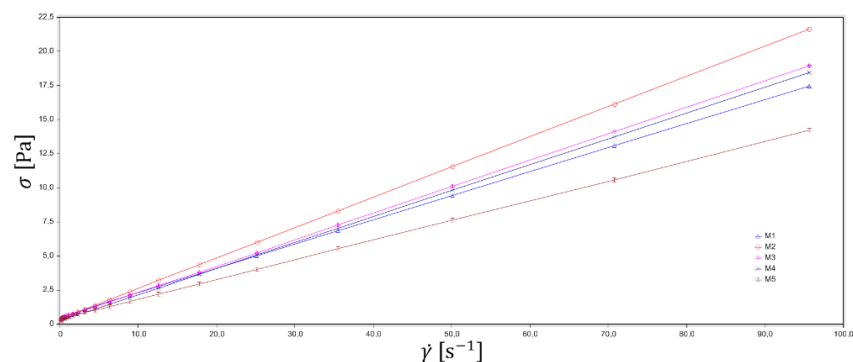


Figure 2. Rheological spectra of pure PVA solution and different SSA loadings of PVA/SSA solutions

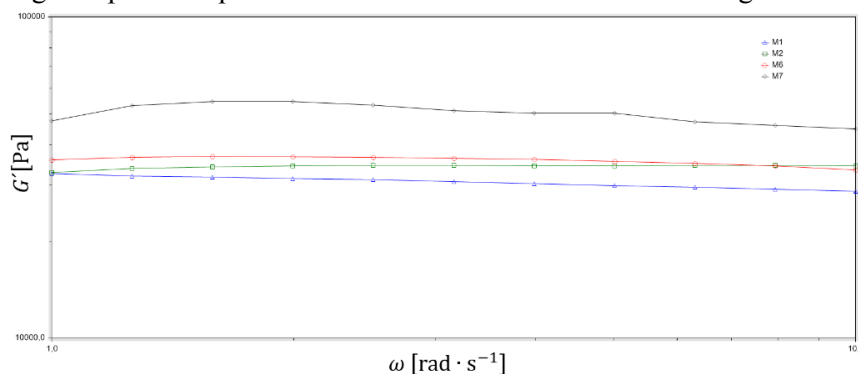


Figure 3. Frequency dependencies of the storage (G') modulus for composite PVA membranes

3.3. TGA

Figure 4 shows thermograms of composite PVA membranes. Thermal stability increases with each additional added component, which means higher crosslinking extents for the composite membrane M2 and for M6 and M7, respectively. This results correspond with rheological properties of modified membranes and show better thermo-mechanical properties of membranes compared to pristine PVA membrane.

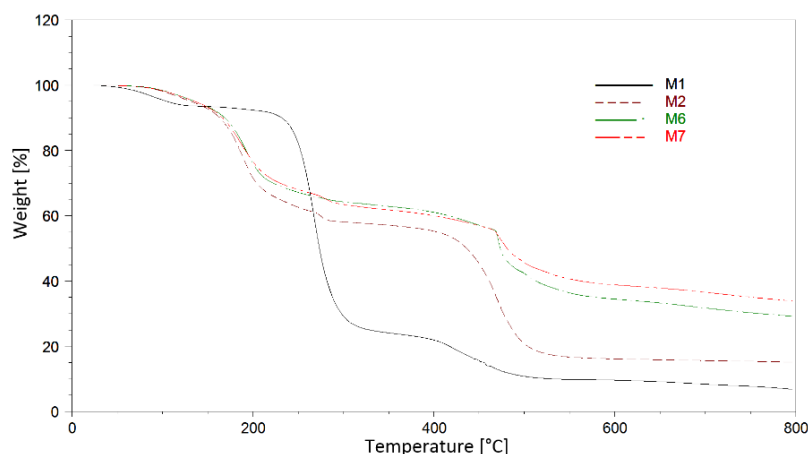


Figure 4. TG thermograms of composite PVA membranes

4. Conclusion

The results of this study can be useful for further research of PVA based composite membranes. Rheological studies show that ideal motion of used SSA is 0.5 wt%. The incorporation of SiO₂ and TiO₂ in the PVA matrix has enhanced the mechanical and thermal properties of membranes.

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